Theory of the Energy Distribution of Photoelectrons*

LEE A. DUBRIDGE, *Washington University, St. Louis, Missouri*

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Because of the thermal energies of the electrons in a metal there can be no *sharply defined* maximum emission energy of photoelectrons, as was once supposed. On the basis of the Sommerfeld theory and the Fermi-Dirac statistics, expressions are derived for the form of the energy distribution and current voltage curves in the vicinity of the apparent maximum energy. The method used is similar to that used by Fowler in computing the total emission current. In Part I the energies normal to the emitting surface are considered. At 0°K the theoretical current-voltage curve is a parabola tangent to the energy axis at V_{max}, while for higher temperatures it approaches the axis asymptotically. In Part II the treatment is extended to the total energy of emission and in this case the current-voltage curve at 0°K is a parabola concave toward the voltage axis and cutting it at a large angle. At higher temperatures there is an asymptotic approach. Even at room temperature there is an uncertainty of several hundredths of a volt in V_{max}, though the theory yields a method of determining the maximum energy which would be observed at 0°K. Both parts of the theory are found to be in agreement with new experiments on molybdenum. The bearing of the theory on the photoelectric determination of h is discussed.

INTRODUCTION

THE problem of the energy distribution of photoelectrons became of great interest to physicists with the propounding of the Einstein equation in 1905. The work of Richardson and Compton,[1] Hughes,[2] Millikan[3] and others has shown clearly that photoelectrons emerge from metal surfaces with all velocities from zero up to a more or less sharply defined maximum velocity, whose value varies with the frequency of the incident light according to the Einstein equation. Since this equation involves only the *maximum* velocity of emission, the attention of physicists working in this field has been largely confined to the problem of measuring this maximum energy with great precision for incident light of different frequencies. Their success in this direction has been so great that the photoelectric method is now regarded as one of the most accurate available for the determination of the value of the universal constant, h/e.

However, it must now be quite generally recognized that there can really be no such thing as a *perfectly sharply defined* maximum emission energy for photoelectrons, except at 0°K, because of the thermal energies of the electrons in the metal. While it might appear at first sight that, at room temperature, the thermal energies would introduce a relatively small uncertainty in the determination of the maximum emission energy, nevertheless even a superficial calculation shows that the uncertainty may be of the order of a few hundredths of a volt. Since the more accurate determinations of h/e have involved measuring the maximum energy to less than 0.01 volt, it becomes of great importance to inquire more in detail as to how much significance can be attached to a "maximum" energy determined with this precision.

In order to answer this problem satisfactorily it is of course necessary to obtain a theoretical expression for the energy distribution function of the photoelectrons and to examine the behavior of this function as it approaches the energy axis. While it is known from experiment that the general form of the distribution curve is that shown in Fig. 1, yet all attempts to deduce a theoretical expression for the curve have met with indifferent success. On the basis of the classical electron theory of metals it was assumed that the kinetic energy of thermal agitation of

* Presented in part at the Chicago meeting of the American Physical Society, November 25, 1932. See Phys. Rev. **42**, 905 (1932).

[1] O. W. Richardson and K. T. Compton, Phil. Mag. **24**, 575 (1912).

[2] A. L. Hughes, Phil. Trans. Roy. Soc. **212**, 205 (1912).

[3] R. A. Millikan, Phys. Rev. **7**, 362 (1916).

the electrons in the metal was negligible in comparison to the energy $h\nu$ received from the incident light, hence it would be expected that *all* electrons would emerge with the *same* velocity, —that given by the Einstein equation,

$$\tfrac{1}{2}mv^2 = h\nu - \phi e,$$

where ϕ is the work function of the surface. The fact, however, that most of the electrons emerged

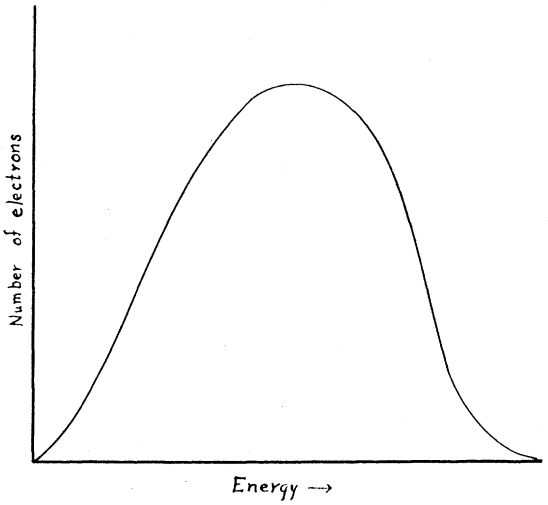

FIG. 1. General form of observed energy distribution curve for photoelectrons.

with a velocity less than this was readily understood on the assumption that the electrons lost energy by collisions within the metal before they reached the surface. However, since the nature of these collisions is unknown, no quantitative expression for the energy distribution can be obtained without introducing special assumptions which cannot be directly tested.

With the advent of the Sommerfeld electron theory it appeared that, because of the long mean free path of the electrons, collision phenomena should play a negligible rôle, and that the energy distribution of the emergent electrons should be directly deducible in terms of the distribution within the metal as given by the Fermi statistics. Fowler[4] has discussed this question qualitatively, but it now appears desirable to attempt a more quantitative treatment.

It should be stated at the outset that at present it is not feasible to attempt to derive a quantitative expression for the complete energy distribution curve, for, granted that collision phenomena may be neglected, it would still be necessary to know (1) the way in which the probability that an electron absorb an incident quantum depends on the initial velocity of the electron itself, and (2) the way in which the transmission coefficient of the electron through the surface potential step W_a depends on the electron velocity. In principle, both factors can be computed from wave mechanics, but the first depends on the detailed structure of the force field within the metal and the second on the exact form of the surface potential step and, for any particular metal, very little is known about either of these. However, as pointed out above, we are not at present interested in the whole form of the distribution curve, but only in its behavior in the vicinity of the "maximum" energy. If we confine our attention to this portion of the curve, it turns out that both above factors vary relatively slowly, and hence can be considered constant. This is particularly true if we also consider only the effect of frequencies near the threshold. Fowler[5] has already made use of these assumptions to derive an expression for the spectral distribution curves in the vicinity of the threshold, obtaining an expression which is in excellent agreement with experiment.[5, 6] It was the remarkable success of Fowler's theory which led the present author to attempt to extend Fowler's methods to the problem of energy distribution.

It will be convenient to divide the treatment of the problem into two parts. In Part I we consider only the energies normal to the emitting surface, since these can be treated simply theoretically and can be readily analyzed experimentally. In Part II the treatment is extended to the total energy of the emitted electrons.

[4] R. H. Fowler, Proc. Roy. Soc. **118**, 229 (1928). A more complete theory for energy distribution from *thin films* has been given by Fröhlich, Ann. d. Physik **7**, 103 (1930).

[5] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[6] L. A. DuBridge and W. W. Roehr, Phys. Rev. **39**, 99 (1932); **42**, 52 (1932); A. H. Warner, Phys. Rev. **38**, 1871 (1931).

I. Distribution of Normal Energies

1. Statement of the problem

Let a plane metal plate A (Fig. 2) be placed in an evacuated bulb and illuminated by light of frequency ν which is greater than the threshold frequency ν_0 (defined below). Let the emitted photoelectrons be collected by a second plate B, parallel to the first, a variable potential being applied between the plates. If B is positive with respect to A, all the emitted electrons are collected and the current is independent of the potential (saturation current). If B has a potential V, negative to A, only those electrons reach B which emerge from A with velocity component v_n, normal to the surface, such that $\frac{1}{2}mv_n^2 = E_n \geqq Ve$. E_n is called for brevity the "normal energy." (In all that follows it will be assumed that the contact potential between the two surfaces has been included in V, so that V is the *actual*, not the *applied*, retarding potential.) Let $F(V)$ be the number of electrons reaching B when the retarding potential is V. If $F(V)$ is measured as a function of V a "current-voltage curve" of the form shown by curve I in Fig. 3 is generally obtained.[7]

Now let V' be the potential required just to stop an electron whose energy is E_n, so that V' is simply E_n expressed in equivalent electron-volts. Let $f(V')dV'$ be the number of electrons emerging with a normal energy V' in the range

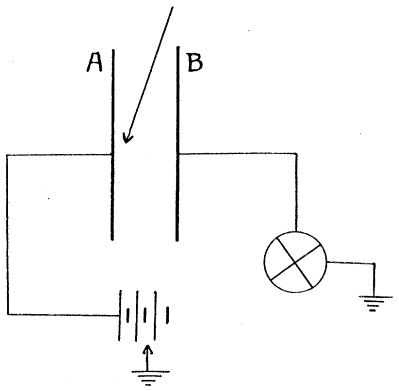

Fig. 2. Parallel plate method.

[7] For a summary of the experimental data see Hughes and DuBridge, *Photoelectric Phenomena*, pp. 11–22 and 114–135.

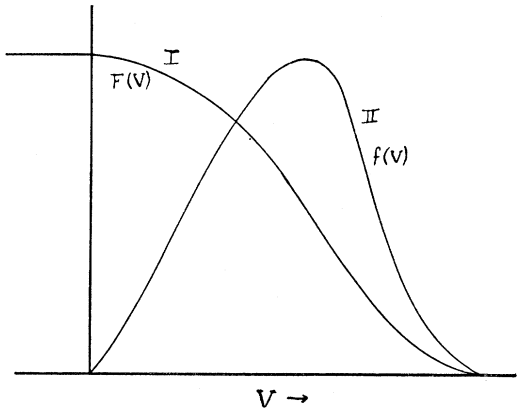

Fig. 3. General form of observed current-voltage curve (I) and the derived energy distribution curve (II).

dV'. Then $f(V')$ is the distribution function for normal energies. Obviously,

$$F(V) = \int_V^\infty f(V')dV' \tag{1}$$

and hence,

$$f(V') = -[dF(V)/dV], \tag{2}$$

the derivative being taken at the point where $V = V'$. Or we may write simply

$$f(V) = -dF(V)/dV.$$

Plotting $f(V)$ against V will then give a curve of the form shown by curve II of Fig. 3.[8]

We will assume:

(1) That the number of electrons per unit volume within the metal having a total kinetic energy ϵ in the range $d\epsilon$ is given by the Fermi-Dirac function

$$n(\epsilon)d\epsilon = \frac{8\pi(2m^3)^{\frac{1}{2}}}{h^3} \frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^{-(\mu-\epsilon)/kT}+1}. \tag{3}$$

(2) That the illuminated surface is perfectly plane and characterized by a surface potential step W_a.

(3) That the chance of an electron absorbing a quantum $h\nu$ is independent of ϵ.

[8] In these curves and some of those that follow as well as in the theory, *retarding* potentials are for convenience taken as *positive*, contrary to usual practice. The derived distribution curves then give energy increasing to the right, as usual.

(4) That the ability of an electron to escape from the surface depends only on its kinetic energy ϵ_n' perpendicular to the surface, where

$$\epsilon_n' = \epsilon_n + h\nu.$$

(5) That the probability that an electron which comes up to the surface with the normal energy ϵ_n' shall actually escape is proportional to the transmission coefficient $D(\epsilon_n')$, and that $D=0$ for $\epsilon_n' < W_a$ and $D=1$ for $\epsilon_n' > W_a$.

2. Energy distribution at 0°K

On the basis of the Fermi statistics, Fowler and Nordheim[9] have shown that the number of electrons reaching unit area of a surface within the metal in unit time with a normal energy between ϵ_n and $\epsilon_n + d\epsilon_n$ is given by

$$n(\epsilon_n)d\epsilon_n = (4\pi mkT/h^3)\log_e[1+\exp(\mu-\epsilon_n)/kT]d\epsilon_n. \quad (4)$$

For $T=0$°K this reduces to

$$n_0(\epsilon_n)d\epsilon_n = (4\pi m/h^3)(\mu-\epsilon_n)d\epsilon_n. \quad (5)$$

$n(\epsilon_n)$ is plotted as a function of ϵ_n in Fig. 4. At absolute zero there are no electrons with an energy greater than μ, hence the least frequency of light, ν_0, which will give electrons energy sufficient to escape is given by

$$\mu + h\nu_0 = W_a \quad \text{or} \quad \nu_0 = (W_a-\mu)/h = \phi e/h. \quad (6)$$

This equation defines the *true* threshold frequency ν_0 and the *true* work function ϕ. As Fowler has shown,[5] for temperatures above absolute zero there is no sharply defined "threshold frequency," though he has developed a method by which ν_0 may be determined from measurements made at any temperature.

If the surface is illuminated by light of a frequency ν which is greater than ν_0, then an electron which originally had the normal energy ϵ_n will emerge with the energy E_n given by

$$E_n = \epsilon_n + h\nu - W_a. \quad (7)$$

We now assume that the number of electrons which emerge with the energy E_n in the range dE_n is proportional to the number coming up to the surface with the energy ϵ_n in the range $d\epsilon_n$. This involves simply assumptions (3), (4) and (5) mentioned above, together with the additional assumption that the energy $h\nu$ acquired from the light is also normal to the surface and so contributes directly to E_n. At first sight this last assumption might appear to be unjustified, since the energy acquired from the light might be in any direction. However, since we are confining our attention to the effect of frequencies not far from the threshold, the only electrons which escape will be those which do acquire energy from the light in a direction nearly normal to the surface, and particularly will this be true for the fastest of the emerging electrons. Hence for the cases we are considering the assumption introduces no appreciable error. If then $f_0'(E_n)dE_n$ is the number escaping with the normal energy E_n in the range dE_n we have at once from Eqs. (5) and (7),

$$f_0'(E_n)dE_n = \alpha(4\pi m/h^3)[\mu-(E_n-h\nu+W_a)]dE_n,$$

where α is a proportionality constant. Or setting $E_n = V'e$ and $W_a-\mu=\phi e$, we have

$$f_0(V')dV' = \alpha(4\pi me/h^3)[(h\nu-\phi e)-V'e]dV'. \quad (8)$$

This is the expression for the distribution of normal energies at the absolute zero, and yields

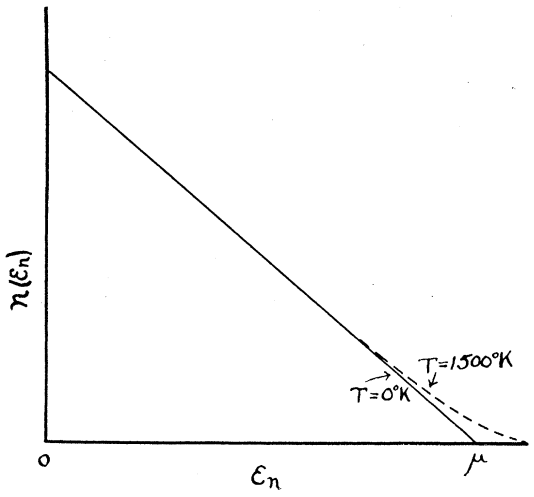

FIG. 4. Fermi-Dirac distribution of normal energies.

[9] R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928); L. Nordheim, Phys. Zeits. **30**, 177 (1929). In plotting $n(\epsilon_n)$ Nordheim made an error which has been corrected in Fig. 4. The curve for $T=1500$°K can at no place fall *below* the 0°K curve, as is shown in his figure.

a distribution curve of the form shown in Fig. 5. It is evident that at this temperature there is a definite maximum energy of emission given by

$$eV_m' = E_{n_m} = h\nu - \phi e, \tag{9}$$

which is the Einstein equation.

Eq. (8) may at once be integrated to give the voltage current curve,

$$F_0(V) = \int_V^\infty f_0(V')dV' = \alpha(2\pi me^2/h^3)(V_m - V)^2, \tag{10}$$

which is the parabola shown by curve II of Fig. 5.

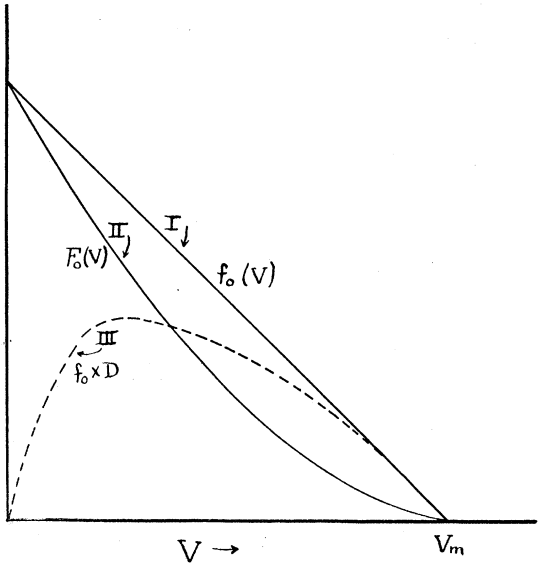

FIG. 5. I. Theoretical distribution of normal energies at 0°K. II. Current-voltage curve. III. Energy distribution corrected for transmission coefficient.

Evidently the curves predicted by this simple theory do not resemble at all, in their general form, the curves actually obtained from experiment. This is largely due to the fact that we have neglected any possible variation of the transmission coefficient D for electrons of different velocities. It is unfortunate that there is no direct method of determining D for any particular surface. However, if we use the values of D computed by Condon[10] and Nordheim[11] for a potential barrier of the form shown in Fig. 6, the energy distribution curve takes the form shown by curve III in Fig. 5, which more nearly resembles the experimental curves, though no quantitative comparison can be made. The point of interest at present, however, is the fact that for electrons emerging from the surface with energies exceeding a few tenths of a volt, D is very nearly unity, and hence does not affect the form of the distribution curve in the vicinity of V_m. This portion of the curve is, however, greatly affected by the temperature of the surface and this effect will now be examined more in detail.

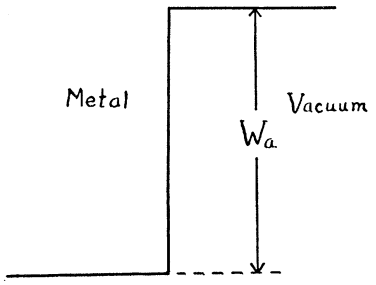

FIG. 6. Ideal surface potential step.

3. Effect of temperature

We have seen above that for a metal at 0°K there is a sharp upper limit to the energy of the emergent photoelectrons, and this varies with the frequency according to the Einstein equation. At higher temperatures, however, there is no longer a sharp upper limit to the energies of the electrons within the metal, and hence no sharp upper limit for the emergent energies, so that the photoelectric current-voltage current curves will have a "tail," and will approach the axis asymptotically. It is possible to deduce a quantitative expression for the form of this tail which can be compared directly with experiment. For this purpose we return to Eq. (4) which is the general expression for the normal energy distribution within the metal, applicable to any temperature. We again use Eq. (7), which states that only those electrons will be able to reach the collecting plate against a retarding potential V which come up to the surface within the metal with a normal energy ϵ_n greater than the critical value ϵ_{n_0}, where $\epsilon_{n_0} = W_a + Ve - h\nu$. The total number, N, of such electrons reaching unit area of the surface in unit time is given by

[10] E. U. Condon, Rev. Mod. Phys. 3, 43 (1931).
[11] L. Nordheim, reference 9.

$$N=\int_{\epsilon_{n_0}}^{\infty} n(\epsilon_n)d\epsilon_n.$$

We will again assume that the number actually reaching the collector is proportional to N. If we write for brevity $W_a'=W_a+Ve$ and use the expression for $n(\epsilon_n)$ of Eq. (4) we have

$$F(V)=\beta(4\pi mkT/h^3)\int_{(Wa'-h\nu)}^{\infty} \times \log_e\left[1+\exp\left([\mu-\epsilon_n]/kT\right)\right]d\epsilon_n, \quad (11)$$

where β is a proportionality constant.

Now the above integral is precisely the one evaluated by Fowler[5] in computing the *total* number of electrons ejected by the frequency ν, except that in the lower limit W_a is replaced by W_a'. This is to be expected, since the effect of a uniform retarding field is simply to increase the effective potential barrier against which the electrons must escape. Fowler's result is, in our present notation,

$$F(V)=\beta\{2(2)^{\frac{1}{2}}\pi m^{\frac{3}{2}}k^2T^2/h^3[W_a'-h\nu]^{\frac{1}{2}}\}\Phi_1(x), \quad (12)$$

where

$$x=(h\nu-[W_a'-\mu])/kT$$
$$=(h\nu-[W_a+Ve-\mu])/kT=e(V_m-V)/kT, \quad (13)$$

and

$$\Phi_1(x)=e^x-e^{2x}/2^2+e^{3x}/3^2-\cdots \quad \text{for } x\leqq 0$$
$$=\pi^2/6+x^2/2-(e^{-x}-e^{-2x}/2^2+e^{-3x}/3^2-\cdots) \quad \text{for } x\geqq 0.$$

Eq. (12) for the voltage-current curve can be compared with experimental curves by a method similar to that used by Fowler. For this purpose the equation may be written in the form

$$\log(F/T^2)=B+\Phi(x). \quad (14)$$

where B is a constant and $\Phi(x)=\log_{10}\Phi_1(x)$. Now $\Phi(x)$ is a universal function of x, the form of the function being shown in Fig. 8 below. If the observed current-voltage curve is plotted in the form $\log(I/T^2)$ as a function of $(-Ve/kT)$ the resulting curve should be of the same shape as the theoretical curve, and should, after a shift parallel to itself, be superposable on it. The amount of the vertical shift is unimportant, depending on the constant B, the intensity of the light, and the units used. The horizontal shift, however, should be equal to eV_m/kT where $eV_m=h\nu-\phi e$, so that V_m is the maximum energy of emission which would be observed if the metal surface were at 0°K. If V_m is determined in this way for a series of frequencies the values should be found to fit the Einstein equation. This method of testing the equation is free from the uncertainty involved in an arbitrary extrapolation of an observed curve which really approaches the axis asymptotically.

4. Experimental test

Experiments are now being conducted by the writer, in collaboration with Dr. R. C. Hergenrother of this laboratory, to test the above theory. A detailed account of these experiments will be published in the near future, after more complete data have been obtained. The results obtained so far, however, furnish a convincing verification of the theory. The details of the experimental technique need not be described here. Suffice to say that the parallel-plate arrangement of the electrodes was used, the photoelectrons being ejected from a thoroughly outgassed strip of molybdenum. The collecting plate is of nickel, which when outgassed has a work function sufficiently high that it is photoelectrically insensitive to the wave-lengths used. The incident light is resolved by a Hilger monochromator with suitable filters to remove scattered light of short wave-length. While the apparatus is designed to allow measurements to be carried out at any temperature of the molybdenum, only the room temperature measurements have so far been completed.

The current-voltage curves, plotted in the usual way, for four different wave-lengths, are shown in Fig. 7. The portion of these curves in the vicinity of the saturation current is not of interest, since the theory does not apply to this portion and since experimentally it is distorted by reflected electrons. Therefore in the figure only the "tails" of the curves are shown, except that in the inset the complete curve for λ2536 is plotted. The portion of this curve plotted to the large scale below is that to the left of the line A. These curves show clearly the predicted asymptotic approach to the axis. The result of analyzing

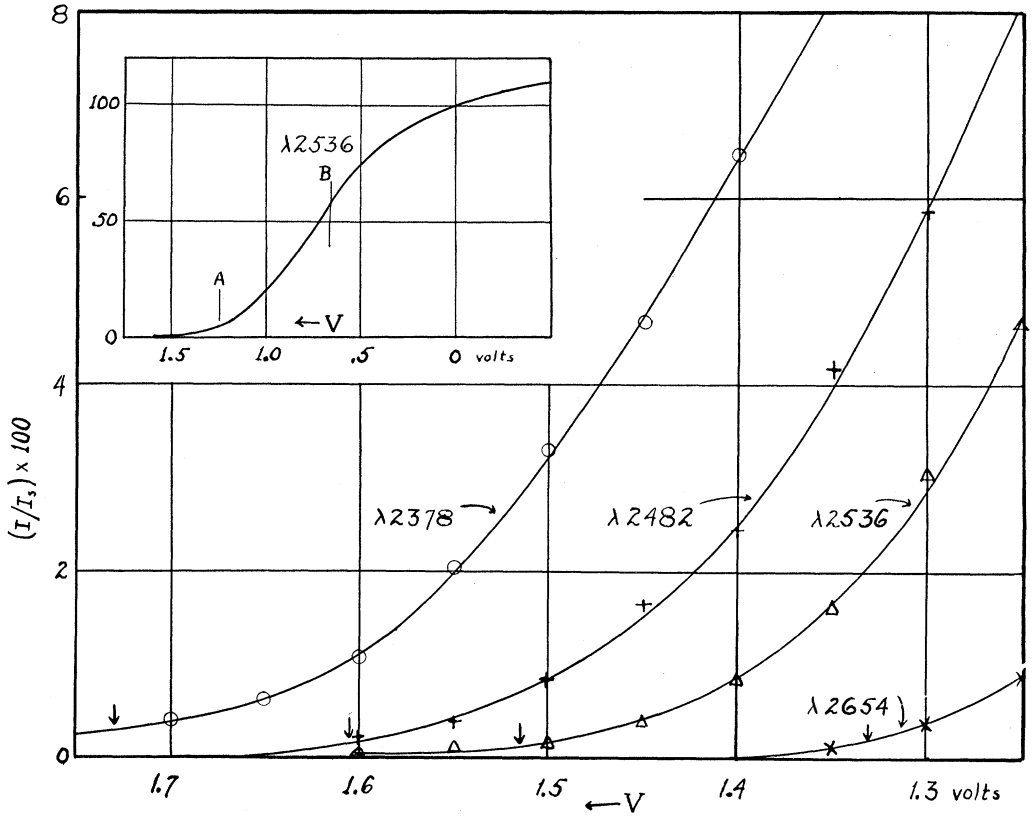

FIG. 7. Experimental current-voltage curves for Mo at room temperature, using parallel plate electrodes. Inset, complete curve for λ2536. Lower curves, magnified portion of the tail. I_s=saturation current. Arrows indicate values of V_m for 0°K.

these curves by the method outlined in the previous section is shown in Fig. 8. The full line is the theoretical curve, and the experimental points are shown after each observed curve has been shifted by the proper amount. The agreement with the theory is well within the limits of experimental error. The portion of the observed curve which can be made to fit the theoretical is roughly that to the left of line B in the inset of Fig. 7, so that the theory predicts the proper shape for the whole lower half of the curve.

From the horizontal shifts required to bring any experimental curve into coincidence with the theoretical, one can determine V_m, the maximum emission energy at 0°K, for that wave-length. The positions of the maximum energies so determined are indicated by the arrows in Fig. 7. If the curves in this figure were extrapolated in the usual way to determine V_m, values greater by several hundredths of a volt would be obtained. It is evident, therefore, that even at room temperature the thermal energies of the electrons are sufficiently important to introduce an uncertainty of this amount into the determination of V_m by the extrapolation method. The experiments have not as yet been carried to sufficient precision to allow an accurate determination of h/e. Nevertheless, the differences between the values of V_m for the different wave-lengths, as determined by the new method, agree roughly with the theoretical values predicted by the Einstein equation. Thus for the two lines 2482A and 2653A the difference between the values of V_m is 0.27 volt, while the corresponding value of $(h/e)(\nu_1-\nu_2)$ is 0.32 volt. The difference can undoubtedly be traced to small changes in contact potential between the emitting and collecting surfaces.

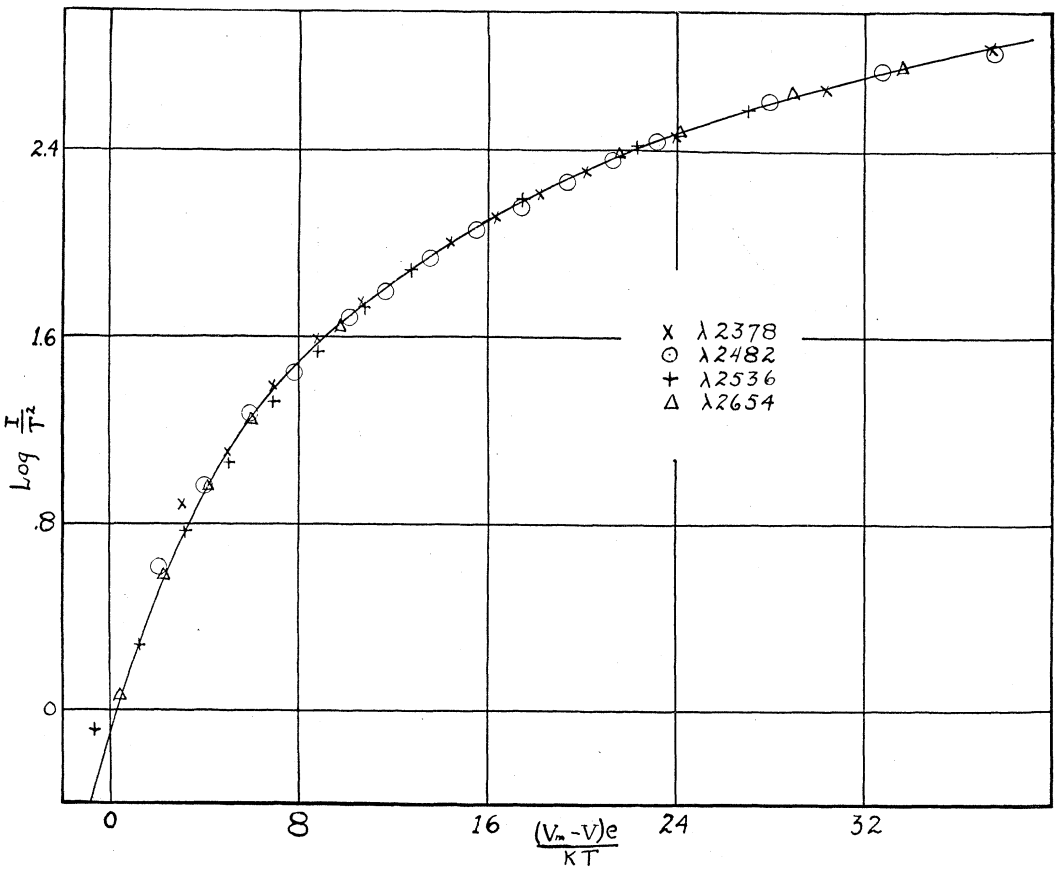

FIG. 8. Analysis of current-voltage curves for Mo.

II. DISTRIBUTION OF TOTAL ENERGIES

5. General statement

While it is possible to analyze the distribution of normal energies of photoelectrons by parallel plate electrodes, most experiments on energy distribution have made use of an arrangement in which the ability of an electron to reach the collecting electrode depended on its *total* energy rather than that normal to the surface. The ideal arrangement for accomplishing this is to have the photoelectrons ejected from a small sphere placed at the center of a much larger collecting sphere. It is desirable to deduce an equation for the energy distribution and voltage current curves to be expected in this case. To do this we will make use of assumptions analogous to those used in Part I and use the following notation:

Let the original velocity of an electron within the metal be u_0, whose rectangular components are ξ_0, η_0, ζ_0, where ξ_0 is chosen normal to the illuminated surface. Calling the corresponding energy ϵ_0, we have

$$\epsilon_0 = \tfrac{1}{2}mu_0^2 = \tfrac{1}{2}m(\xi_0^2+\eta_0^2+\zeta_0^2). \quad (15)$$

If the electron absorbs a quantum $h\nu$ it will attain an energy ϵ and a corresponding velocity u with components ξ, η, ζ, such that

$$\epsilon = \tfrac{1}{2}mu^2 = \tfrac{1}{2}m(\xi^2+\eta^2+\zeta^2) = \tfrac{1}{2}mu_0^2+h\nu. \quad (16)$$

If such an electron comes up to the surface with a velocity u whose component perpendicular to the surface ξ is greater than some critical value ξ_c, where $\frac{1}{2}m\xi_c^2 = W_a$, the electron may escape from the surface with the energy loss W_a. Let v be the total velocity of escape and E the corresponding energy; and call the component of v normal to the surface v_n. Then we will have

$$E = \tfrac{1}{2}mv^2 = \tfrac{1}{2}mu^2 - W_a = \tfrac{1}{2}m(u^2-\xi_c^2) \quad (17)$$

and

$$\tfrac{1}{2}mv_n^2=\tfrac{1}{2}m(\xi^2-\xi_c^2). \tag{18}$$

At the absolute zero the maximum energy with which an electron can come up to the surface is $(\mu+h\nu)$. Hence the maximum velocity of escape, v_m, and the corresponding maximum energy E_m will be given by the Einstein equation, as before,

$$\tfrac{1}{2}mv_m^2=E_m=h\nu-(W_a-\mu). \tag{19}$$

Since we will be continually using the Fermi-Dirac distribution function it will be convenient to make the following abbreviations: Let

$$\Psi(u_0)=\frac{1}{e^{(\frac{1}{2}mu_0^2-\mu)/kT}+1}. \tag{20}$$

Substituting for u_0 its value in terms of u from Eq. (16) we have

$$\Psi(u)=\frac{1}{e^{(\frac{1}{2}mu^2-h\nu-\mu)/kT}+1}. \tag{21}$$

Or finally in terms of v, from Eq. (17),

$$\Psi(v)=\frac{1}{e^{(\frac{1}{2}mv^2+W_a-h\nu-\mu)/kT}+1} \tag{22}$$

$$=\frac{1}{e^{(E-E_m)/kT}+1}.$$

6. General equation for energy distribution

The number of electrons per unit volume within the metal having total velocities between u_0 and u_0+du_0 is given by the Fermi-Dirac function

$$n(u_0)du_0=(8\pi m^3/h^3)u_0^2\Psi(u_0)du_0, \tag{23}$$

where $\Psi(u_0)$ is defined by Eq. (20). When the surface is illuminated a certain fraction, p, of these electrons will absorb the energy $h\nu$ attaining thereby the velocity u in the range du, where,

$$u^2=u_0^2+2h\nu/m,$$

and hence

$$udu=u_0du_0.$$

The number of electrons per unit volume having the velocity u in the range du will then be

$$n(u)du=(8\pi m^3/h^3)p[u^2-(2h\nu/m)]^{\frac{1}{2}}u\Psi(u)du. \tag{24}$$

Of these electrons only those can escape which have velocity components normal to the surface greater than the critical value ξ_c defined above. But since the velocities are equally distributed in all directions, it can readily be shown that the fraction of the total number of electrons having the velocity u, whose velocities are directed in such a way that the component normal to the surface is equal to or greater than ξ_c is $\frac{1}{2}(1-\xi_c/u)$. If we multiply $n(u)$ by this factor, and also by ξ, we get the number coming up to unit area of the surface per second with energies sufficient to escape. Multiplying then by the transmission coefficient $D(u)$, we get the number actually escaping. Now electrons which come up to the surface with the velocity u in the range du and escape will emerge with the velocity v in the range dv, and from Eq. (17) we have

$$v^2=u^2-\xi_c^2$$

$$vdv=udu.$$

Hence the number escaping per second with velocities in the range between v and $v+dv$ is given finally by

$$N(v)dv=(8\pi m^3/h^3)p\xi D(v)[v^2+\xi_c^2-2h\nu/m]^{\frac{1}{2}}\cdot\tfrac{1}{2}[1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]v\Psi(v)dv, \tag{25}$$

where $\Psi(v)$ is defined by Eq. (22).

Eq. (25) is the general equation for the *velocity* distribution of the emitted electrons, in which no approximations have been made. The equation can be greatly simplified by making approximations of the same order as in Part I. This involves assuming that the factor p is constant and that $D(v)=1$. In addition, if ν is not too far from the threshold ν_0, the factor ξ will not differ greatly from ξ_c and hence may be assumed constant. Also we will have $u^2=(v^2+\xi_c^2)\gg 2h\nu/m$, so that the first factor in the brackets may be expanded and second order terms neglected, giving,

---

$$[(v^2+\xi_c^2)-2h\nu/m]^{\frac{1}{2}}=(v^2+\xi_c^2)^{\frac{1}{2}}-[h\nu/m(v^2+\xi_c^2)^{\frac{1}{2}}].$$

Now this is to be multiplied by the second factor in brackets. The first term of the product may be expanded as follows

$$(v^2+\xi_c^2)^{\frac{1}{2}}[1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]=(v^2+\xi_c^2)^{\frac{1}{2}}-\xi_c=v^2/2\xi_c=\alpha v^2,$$

since $v^2\ll\xi_c^2$, α being a constant $=1/2\xi_c$. The second term gives, similarly,

$$[h\nu/m(v^2+\xi_c^2)^{\frac{1}{2}}][1-\xi_c/(v^2+\xi_c^2)^{\frac{1}{2}}]=[h\nu/m(v^2+\xi_c^2)](v^2/2\xi_c)=\beta v^2,$$

where β, the coefficient of v^2, can be considered essentially constant, since $v^2\ll\xi_c^2$ and only small ranges of v are to be considered. Making use of the above results, and of Eq. (22), we have finally from Eq. (25)

$$N(v)dv=A''\frac{v^3dv}{e^{(E-E_m)/kT}+1}. \tag{26}$$

$$A''=\text{const.},$$

as our final equation for the *velocity* distribution. Making now the substitutions $V'e=(\frac{1}{2})mv^2$ and $edV'=mvdv$ we have for the *energy* distribution function

$$f(V')dV'=A\frac{V'dV'}{e^{(V'-V_m)e/kT}+1}, \tag{27}$$

where $A=A''\cdot 2e^2/m^2$.

In Fig. 9, $f(V')$ is plotted as a function of V' for the temperatures 0°, 300° and 900°K and

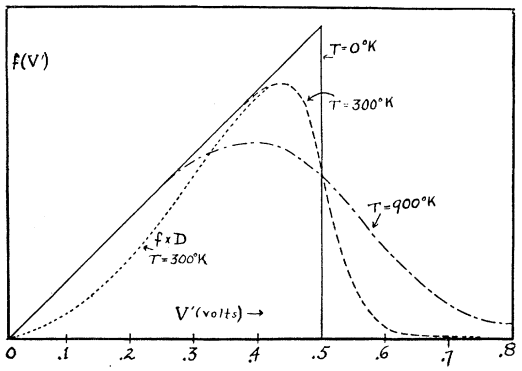

FIG. 9. Theoretical distribution of total energies for three temperatures.

for $V_m=0.5$ volt. It is seen that the sharpness of the "maximum" energy is greatly affected by the temperature. It has been occasionally suggested that the "apparent" maximum energy, determined by an arbitrary extrapolation of a room temperature curve, would be the same as the true maximum energy for 0°K. The curves show, however, that this is far from being the case. It is evident also that the form of the curves is not that usually obtained experimentally. If one corrects, as before, for the variation of the transmission coefficient D, a distribution curve of the form shown by the dotted curve is obtained, which resembles more nearly the experimental curve. However, even with this correction the most probable energy on the theoretical curve is much nearer the "maximum" energy than in most experimental curves. Experiments are now in progress in this laboratory to test the cause of this discrepancy. Some experiments of Bennewitz[12] suggest that the most probable energy shifts to higher values as the surface is outgassed, and our preliminary results show that the curves for *very clean* surfaces more nearly resemble the theoretical curves.[13]

In order to make direct comparison with experiment, however, it is desirable to obtain an expression for the current-voltage curve, in order to eliminate the uncertainties involved in differentiating an experimental curve.

7. Current-voltage curve

If the collecting sphere is at a potential V, negative to the emitting surface, the number of electrons received will be the total number emerging from the surface with energies greater than Ve. Hence

$$F(V)=\int_V^\infty f(V')dV'$$

$$=\int_V^\infty \frac{AV'dV'}{e^{(V'-V_m)e/kT}+1}. \tag{28}$$

This integral may be evaluated by making the substitutions:

$$x=Ve/kT,\quad x'=V'e/kT,\quad dx'=edV'/kT,$$

$$\text{and}\quad x_0=V_me/kT.$$

[12] W. Bennewitz, Ann. d. Physik **83**, 913 (1927).

[13] It should be pointed out that the form of the theoretical curve is similar to that deduced by Fröhlich (Ann. d. Physik **7**, 103 (1930)) for the case of thin films.

Then

$$F(V)=Ak^2T^2\int_x^\infty \frac{x'dx'}{e^{(x'-x_0)}+1}. \tag{29}$$

By making the further substitutions $e^{x'}=w$, $dx'=dw/w$, and $e^{-x_0}=a$, the integral becomes

$$\int \frac{\log w\, dw}{w(aw+1)}. \tag{30}$$

This may be integrated by parts by using standard forms. The form of the result depends on whether x' is greater or less than x_0, so that for the value of the indefinite integral (30) we find

$$F_1=x'(x'-x_0)-\tfrac{1}{2}(x'-x_0)^2-x'\log\left[1+e^{(x'-x_0)}\right]+\left[e^{(x'-x_0)}-e^{2(x'-x_0)}/2^2+e^{3(x'-x_0)}/3^2-\cdots\right], \quad \text{for } x'\leqq x_0.$$

$$F_2=x'(x'-x_0)-x'\log\left[1+e^{(x'-x_0)}\right]-\left[e^{-(x'-x_0)}-e^{-2(x'-x_0)}/2^2+e^{-3(x'-x_0)}/3^2-\cdots\right], \quad \text{for } x'\geqq x_0.$$

In case the applied retarding potential V is less than V_m (i.e., $x<x_0$) we substitute the limits x to x_0 in F_1 and x_0 to ∞ in F_2, then

$$F(V)=Ak^2T^2\{[F_1]_x^{x_0}+[F_2]_{x_0}^{\infty}\}, \quad x\leqq x_0.$$

In case $V>V_m$, i.e., $x>x_0$, we have

$$F(V)=Ak^2T^2[F_2]_x^{\infty}, \quad x\geqq x_0.$$

Substitution of the limits gives

$$F(V)=Ak^2T^2\{\pi^2/6-\tfrac{1}{2}(x^2-x_0^2)+x\log\left[1+e^{(x-x_0)}\right]-\left[e^{(x-x_0)}-(1/2^2)e^{2(x-x_0)}+(1/3^2)e^{3(x-x_0)}-\cdots\right]\}, \quad x\leqq x_0 \tag{31}$$

$$F(V)=Ak^2T^2\{-x(x-x_0)+x\log\left[1+e^{(x-x_0)}\right]+\left[e^{-(x-x_0)}-(1/2^2)e^{-2(x-x_0)}+(1/3^2)e^{-3(x-x_0)}-\cdots\right]\}, \quad x\geqq x_0. \tag{32}$$

For the case $V=V_m$ (i.e., $x=x_0$) either of the above expressions reduces to

$$F(V_m)=Ak^2T^2(x_0\log 2+\pi^2/12), \quad x=x_0.$$

Eqs. (31) and (32) are the final equations for the current voltage curves for the case of spherical electrodes. Before discussing them in detail it is of interest to consider two limiting cases.

(1) For $T=0°\mathrm{K}$ the equations become, on setting $x=Ve/kT$ and $x_0=V_me/kT$,

$$\begin{aligned} F_0(V)&=(Ae^2/2)(V_m^2-V^2) && \text{for } V\leqq V_m \\ F_0(V)&=0 && \text{for } V\geqq V_m. \end{aligned} \tag{33}$$

The current voltage curve at absolute zero is thus a parabola, and there is a sharply defined maximum retarding potential.

(2) For $V=0$, i.e., no retarding potential, $F(V)$ should be equal to the total saturation current. Setting $x=0$ in Eq. (31), we have

$$F(0)=Ak^2T^2\{\pi^2/6+x_0^2/2-\left[e^{-x_0}-e^{-2x_0}/2^2+e^{-3x_0}/3^2-\cdots\right]\}. \tag{34}$$

Remembering that $x_0=V_me/kT=(h\nu-\phi e)/kT=h(\nu-\nu_0)/kT$, this equation is found to be identical with that obtained by Fowler for the total number of electrons ejected from a surface at the temperature T by the frequency ν which is greater than the threshold ν_0. This agreement is to be expected, since the approximations used in the present analysis are of the same order as those employed by Fowler.

It is seen from Eqs. (31) and (32) that $F(V)$ is not a universal function of V as in the case considered in Part I. The form of the curve obtained depends on the absolute value of x_0 $[=h(\nu-\nu_0)/kT]$. That is, for a given temperature the form of the curve will depend on the difference between the incident frequency and the threshold frequency for the particular surface. Or, for a given value of $(\nu-\nu_0)$, or of V_m, the form of the curve depends on the temperature. These effects are seen in Fig. 10, where relative values of $F(V)$ are plotted as a function of x/x_0 for several values of x_0. The curve for $x_0=\infty$ would be obtained at $0°\mathrm{K}$ for any incident

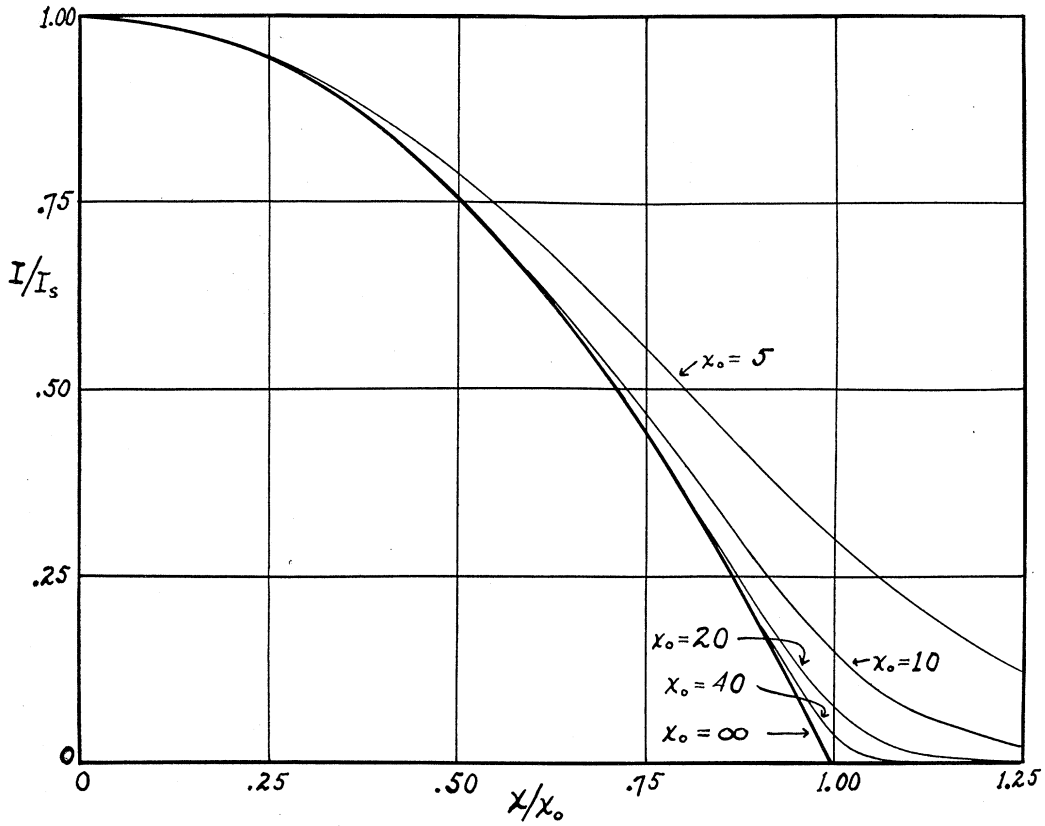

FIG. 10. Theoretical current-voltage curves for various values of x_0, reduced to the same saturation current, I_s.

frequency. It is the parabola given by Eq. (33). For $T=300°K$ the different curves would correspond to values of V_m as follows:

x_0	∞	40	20	10	5
V_m (volts)	∞	1.04	0.52	0.26	0.13

On the other hand, if the incident frequency were chosen so that $V_m=0.5$ volt, for example, the temperatures corresponding to the various curves would be:

x_0	∞	40	20	10	5
$T°K$	0	150	300	600	1200

Although the calculation of a complete $F(V)$ curve from Eqs. (31) and (32) is somewhat tedious, the process is greatly simplified by using the following approximations, which are valid for the regions indicated:

$$F(V)=\tfrac{1}{2}Ak^2T^2[(x_0^2-x^2)+\pi^2/3], \quad \text{for } (x_0-x)>3 \quad (35)$$

$$=Ak^2T^2(x_0\log 2+\pi^2/12), \quad \text{for } (x_0-x)=0$$

$$=Ak^2T^2\{x[e^{-(x-x_0)}-(1/4)e^{-2(x-x_0)}]\}, \quad \text{for } (x_0-x)<-1 \text{ and } x_0>10. \quad (36)$$

Eq. (36) above is not easily deduced analytically, but it was found accidentally in numerical calculation to hold very closely.

8. Experimental test

An experimental test of this portion of the theory is being carried out in this laboratory by Mr. W. W. Roehr, whose results will be published in a later paper. The results so far obtained, however, are again in excellent agreement with the theory.

The experimental set-up in this case is designed to approximate as closely as possible the ideal concentric-sphere arrangement. Photoelectrons are liberated from a small strip of thoroughly

outgassed molybdenum placed at the center of a large collecting sphere. The incident light is resolved by a double quartz monochromatic illuminator which eliminates scattered light of short wave-lengths. Again the apparatus is designed to take measurements at any temperature of the molybdenum, though at present only the room temperature measurements have been completed.

In analyzing these results a somewhat different graphical method has been developed. Referring to Eq. (36), it is seen that the expression for the tail of the theoretical curve (i.e., $x>x_0$) may be written approximately in the form

$$F(V)=Ak^2T^2xf(x-x_0),$$

where $f(x-x_0)$ is a universal function of its argument. This equation may be rewritten in the form

$$\log\,(F/xT^2)=B+f'(x-x_0),$$

where $f'=\log f$. Plotting f' as a function of (x_0-x) gives the curve shown in Fig. 11. If the experimental results are then plotted in the form $\log\,(I/xT^2)$ as a function of x (or, at a fixed temperature, $1/T^2$ may be absorbed in the constant B) the curve obtained should be of the same form as the theoretical curve and, after a shift parallel to itself, should be superposable on it. The amount of the horizontal shift again determines x_0, and hence V_m as before. The results of analyzing the experiments in this way are shown in Fig. 11. Again it is seen that at room temperature the shape of the lower portion of the experimental curve is very closely that predicted by the theory. The complete current-voltage curves, plotted in the usual way, are shown in Fig. 12, with the values of V_m obtained as above indicated by arrows. The difference between the values of V_m for the lines 2536A and 2804A is 0.50 volt, and the corresponding value of $(h/e)(\nu_1-\nu_2)$ is 0.49 volt, the agreement being within the limit of error of the observations. The form of the theoretical curve for 0°K is indicated approximately by the broken lines in Fig. 12. It is seen that in this case the temperature tail gives rise to a considerable uncertainty in the determination of V_m by the extrapolation method.

9. Conclusion

While the verification of the theory presented in this paper will not be complete until the more extended and more accurate measurements now under way in this laboratory are finished, the preliminary results indicate that the theory predicts the correct form of the energy distribution and current-voltage curves in the vicinity of the maximum energy. Aside from giving for the first time a quantitative expression for the form of these curves, one of the chief points of interest in the theory is that it brings out clearly the uncertainty in any determination at ordinary temperatures of the "maximum" emission energy of photoelectrons by the usual extrapolation methods. At the same time it yields a method for determining the true maximum energy at 0°K.

This raises the question as to how it happens that the photoelectric method of determining h (involving an arbitrary extrapolation) has yielded such accurate results in the past. Referring first to the experiments in which the alkali metals were used, such as those of Millikan[3] and of Olpin,[14] the reason for their success can be seen from an examination of the curves of Fig. 10. With alkali metals the value of $(\nu-\nu_0)$, and hence of x_0, may be quite large, up to about 3 volts. The theoretical curve for this case $(x_0\sim 120)$ would practically coincide with the curve labelled $x_0=\infty$, the temperature tail being probably too small to be observed, or at least small enough to be neglected when the extrapolation is made.[15] Hence in this case the extrapolation method would yield practically the value of V_m which would be observed at absolute zero. Millikan purposely ignored the rather large tails to some of his curves, attributing them to the presence of scattered light of short wavelength. While most of the tail was proably due to this cause, this method certainly ignored also a small tail due to thermal energies. The fact that Millikan's experiments yielded the correct value of h while the previous experiments of Hughes[2] and Richardson and Compton[1] did not, may be due in part to the fact that in the latter

[14] A. R. Olpin, Phys. Rev. **36**, 251 (1930).

[15] In the case of the alkali metals also it is no longer true that $\frac{1}{2}mu^2>>h\nu$ and some of the approximations made in the theory would fail, so that the curves of Fig. 10 would have a different form.

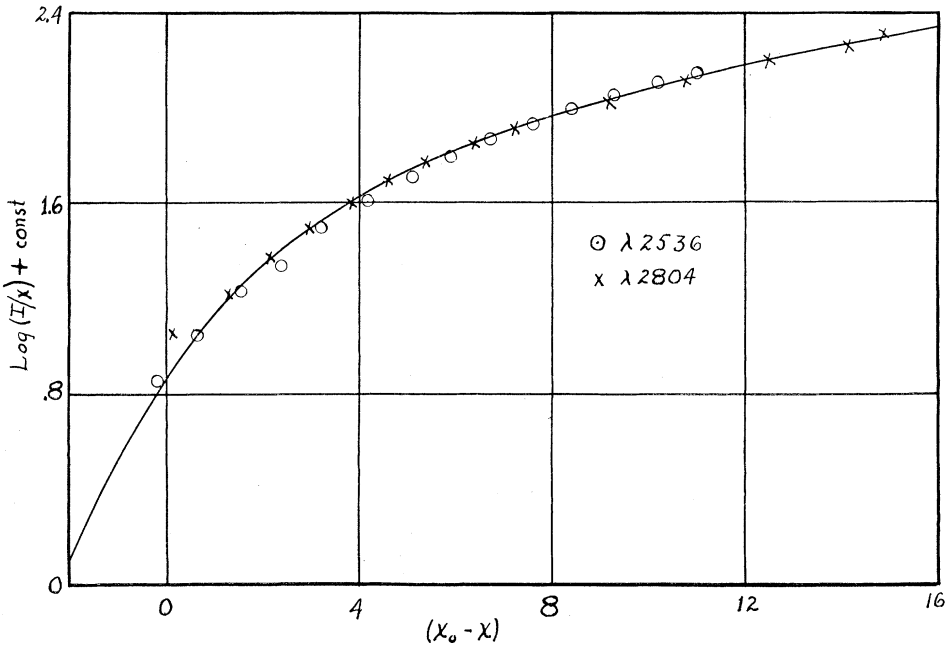

FIG. 11. Analysis of current-voltage curves for Mo at room temperature, using spherical electrodes.

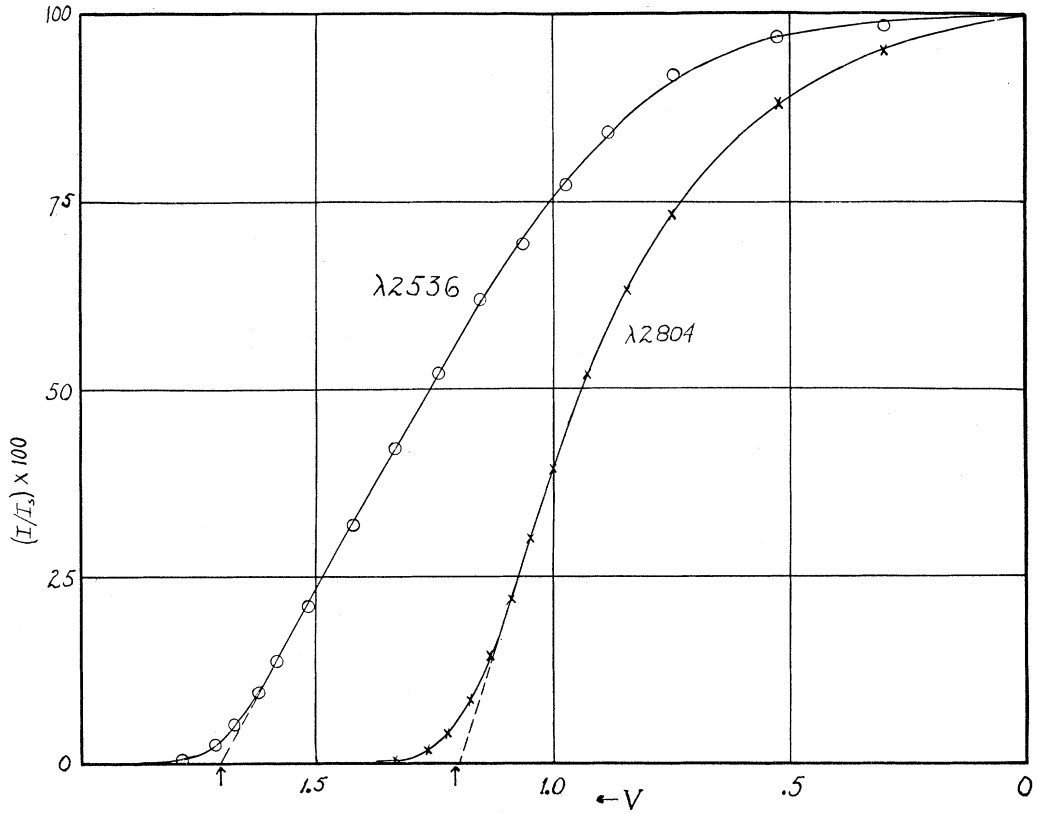

FIG. 12. Observed current-voltage curves for clean Mo. Broken lines indicate approximately the theoretical shape of the tail for 0°K. To avoid congestion only a few of the observed points are plotted.

experiments alkali metals were not used so that the values of $(\nu-\nu_0)$ were small, and hence the temperature effect relatively more important. In this case the extrapolation method fails.

It is more difficult to account for the amazing precision attained in the experiments of Lukirsky and Prilezaev[16] who employed metals such as silver, gold and platinum. For the values of $(\nu-\nu_0)$ which they used the effect of temperature on the tail of the curve is by no means negligible. At room temperature the values of V_m obtained by extrapolation would be from 5 to 25 percent greater than the value of V_m at 0°K. One must apparently assume that a fortunate method of extrapolation was chosen which happened to yield values of V_m which were always greater *by exactly the same amount* than the absolute zero values. This would yield a correct value of h. An alternative explanation may be sought in the fact that their experimental curves were not at all of the form of the theoretical curves of Fig. 10. The evidence at present suggests that this is due to the fact that they made no attempt to outgas the illuminated surfaces. The presence of gas in a surface might alter the form of the surface potential barrier or, more probably, affect the collision phenomena within the metal, in such a way that the assumptions made in our theory no longer apply. This might alter the shape of the current-voltage curve so as to make the temperature effect relatively less important. Even in this case, however, it is very difficult to understand how values of V_m *consistent among themselves to 0.001 volt* (as is claimed) could be obtained except as a result of an exceedingly fortuitous extrapolation method.

In conclusion the author wishes to express his indebtedness to Dr. R. C. Hergenrother and Mr. W. W. Roehr who have carried out the experimental work described here, and to acknowledge that this work was made possible through an appropriation to the author from a grant made by the Rockefeller Foundation to Washington University for research in science.

[16] P. Lukirsky and S. Prilezaev, Zeits. f. Physik **49**, 236 (1928).